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The University of Southern Mississippi

Kinetic Study of Conjugated
Polymer Packing and Agglomeration

by

Skye Travis

A Thesis
Submitted to the Honors College of
The University of Southern Mississippi
in Partial Fulfillment
of the Requirements for the Degree of
Bachelor of Science in Chemistry
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Abstract

Although organic electronic materials are flexible, cheap to fabricate, and molecularly tunable, their performance has generally been less efficient than that of their inorganic counterparts. Chemical doping has been attempted as a method to increase the efficiency of organic materials. During this process, an organic material, typically a conjugated polymer, is exposed to an oxidant/reductant, called a dopant. Electron transfer between host polymer and dopant molecules increases the charge carrier density in the doped host material, making it a more efficient conductor. The effects of doping using 2,3,5,6-tetrafluoro-tetracyanoquinodimethane (F4TCNQ) on low molecular weight poly(3-hexylthiophene-2,5-diyl) (LMW P3HT) in varying ratios of a decane/toluene solvent was investigated. Increasing the fraction of decane, a nonpolar bad solvent that does not facilitate charge transfer, forces the P3HT to aggregate very quickly. A comparison is made between the UV-vis spectra of samples prepared with decane and those of samples prepared in pure toluene. By comparing the chemical doping behavior between aggregated and non-aggregated forms of P3HT, the influences of P3HT aggregation on their chemical doping kinetics are elucidated. The experimental results obtained support the hypothesis that P3HT must undergo its aggregation step before a doping product can be formed.

Key words: P3HT, F4TCNQ, doping kinetics, aggregation

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List of Abbreviations

F4TCNQ	2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane
P3HT	Poly(3-hexylthiophene-2,5-diyl)
CP	conductive polymer
D-A-D	donor-acceptor-donor
PHTBT	poly (2-dodecyl-4 ,7-bis (4-hexiltiofen-2-yl)-2H-benzo[d] [1,2,3] triazole)
NMR	nuclear magnetic resonance
DPP	diketo pyrrolo-pyrrole
PBTTT-C14	Poly[2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2-b] thiophene]
CNFET	carbon nanotube field-effect transistors
LMW	low molecular weight
UV-vis	ultraviolet-visible spectroscopy
s-P3HT	solubilized P3HT
nw-P3HT	nanowire P3HT (aggregated species)
HMW	high molecular weight

Chapter 1: Introduction

Technology is advancing faster than ever before. In the past twenty years, the world has stopped viewing the Internet as being this vast new place. Today, most people carry a supercomputer in their pockets. Because of this, researchers are questioning why we use the same materials for our electronics that have been the norm for decades. Currently there are numerous attempts to explore the possibility of using organic, or carbon-based, electronics. This introduces opportunities to create cheaper and more flexible alternatives to the more common inorganic counterparts for a variety of applications, including solar cells, transistors, and display devices.

The conductivity of organic electronic materials thus far has been lower than the inorganic versions, but researchers are trying to find a way to address that issue by using a method called chemical doping. This method consists of the organic electronic material, typically a conjugated polymer, being “doped,” or exposed, to an oxidative or reductive chemical compound called a dopant. Electron transfer between the host polymer and dopant molecules increases the charge carrier density in the doped host material, making it a more efficient conductor. Studying the effects of doping and how it changes the polymer can give great insight to the doping process and mechanisms. This can be done by performing a kinetic study, a study of the rates of the reactions, of the processes being studied.

This thesis focuses on how a dopant reacts with a specific species of polymer in different solvents. I determine how the dopant 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) reacts with Poly(3-hexylthiophene-2,5-diyl) (P3HT). This research used physical chemistry experimentation to produce a study of the

polymer species reacting to the chosen dopant to elucidate the effect of polymer packing on its doping reaction kinetics.

Chapter 2: Literature Review

Researchers have been studying conductive polymers for years. Recently, the understanding of the electrochemistry involved in the charging of conductive polymers (CPs) has come a long way¹. Experimentation has revealed that some hypotheses put forth in old literature are highly unlikely, like the hypothesis that a chain propagation mechanism was at play¹. There has even been evidence that CPs act like molecular systems. Although it happens rarely, evidence also supports the existence of bipolarons, a part of a macromolecular chain with two positive charges, which are predicted by the band model, a diagram used to predict the behavior of electrons within a system.¹ Because of this new knowledge, researchers are closer than ever to being able to create efficient organic electronic materials.

It is not uncommon that the usage of a new polymer will increase the efficiency of an organic electronic device, such as an organic solar cell. In fact, in an experiment conducted by Baran et al., the D-A-D (donor-acceptor-donor) type polymer poly (2-dodecyl-4,7-bis (4-hexylthiophen-2-yl)-2H-benzo[d] [1,2,3] triazole), referred to as PHTBT, was found to increase the open circuit voltage of a solar cell up to 0.85 V when it was used as the donor material.² Sometimes the polymer is used in a semiconductor/insulator blend due to both higher performance and environmental stability. However, synthesis and purification of a new polymer compound is typically expensive and time-consuming, which calls for an easier way to improve CP's properties. Doping could potentially enhance the performance of such mixtures or add new functions. For example, using a dye doping method, some conjugated polymer nanoparticle tags can be easily characterized with optical techniques³. Most polymers, however, undergo chemical

doping with chemical dopant molecules to enhance their conductivity. Conductivity, the capability of a material to transport an electric current, is an important factor to consider for a semiconductor polymer. A polymer blend, in its undoped state, performs quite poorly, having limited mobility⁴. When a dopant is introduced, the charge transfer reaction produces an extra host molecule ion that can function as a charge carrier, which improves these characteristics drastically.⁴

Doping is not the only thing that determines the properties of a polymer-based device. One must also take the packing of the polymer into consideration. Packing is the spatial arrangement of polymer molecules. In an experiment by Dudenko et al., the packing of a π -conjugated polymer such as P3HT was studied by multi-technique crystallography.⁵ This method is comprised of several different analytical methods, including x-ray diffraction and solid-state nuclear magnetic resonance (NMR). Packing, of course, is different for different kinds of polymers, and the packing orientation can even change between various specific polymers within a certain variety. For example, in diketopyrrolo-pyrrole (DPP) based polymer semiconductors, the preferred orientation changes from edge-on to face-on as the side chain attachment density increases.⁶ Side chain attachment density correlates to the amount of space between side chains of a polymer. As the density increases, space between the side chains decreases. The most efficient way for a polymer blend to be packed would seem to be in a cofacial arrangement. This conformation, at least in the case of a F4TCNQ and Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT-C14) blend, creates an electron transfer efficiency of nearly 100% in the solid state. This would suggest that the locations of molecular acceptors should be correlated instead of dispersed randomly.⁷

One of the major downfalls of polymer-based electronic materials, specifically solar cells, is the fact that their efficiency is directly linked to the nanoscale morphology of the thin active layer. When the layer absorbs light, an electron-hole pair, also called a Coulombically bound exciton, is formed. Particles in a lower dielectric medium (a medium with a high insulation ability), like a polymer matrix, have a higher binding energy. This means that the electron-hole pair will not stay in the excited state for as long, and the excitation diffusion length in low dielectric media is shortened, limiting efficiency of the eventual solar cell.⁸ High agglomeration can also negatively affect the properties of some polymer nanocomposites. A lot of clustering can cause loss of volume and blocks percolation networks, or random pathways, from forming within the composite.⁹

This thesis describes research using the dopant F4TCNQ. This is a common p-dopant in work on organic electronic materials, and is found to be effective at increasing device performance in carbon nanotube field-effect transistors (CNFETs) by improving transconductance.¹⁰ The polymer used in this research, P3HT, is one of the most widely used conjugated polymers for organic electronic materials because of its high charge carrier mobility. It is possible for P3HT to undergo a crystalline phase involving F4TCNQ being brought into structured regions when the dopant concentration is higher than a critical point, which increases carrier density in thin films.¹¹ Literature about F4TCNQ and P3HT shows that the two compounds work well together¹¹, possibly due to their integer charge transfer during doping.

The exact mechanisms of doping of P3HT by F4TCNQ are not well understood. This thesis investigates the doping mechanism of P3HT with F4TCNQ with specific

attention to the effects of the polymer packing on the doping mechanism. There are three possible mechanisms by which chemical doping could occur for this system, shown in Figures 1-3. In the first mechanism, the P3HT will charge transfer with F4TCNQ, and the resulting P3HT polaron will aggregate. In the second mechanism, both charge transfer and aggregation occur simultaneously. In the third and final possible mechanism, the packing step occurs before the charge transfer can take place. In this thesis, by experimentally examining the doping reaction of P3HT with F4TCNQ, their doping reaction mechanism will be elucidated.



Figure 1 - Possible mechanism for doping 1: Charge transfer occurs before aggregation

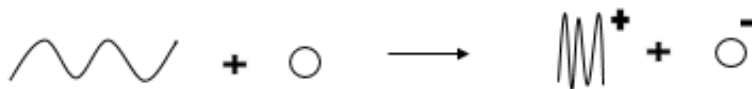


Figure 2 - Possible mechanism for doping 2: Charge transfer and aggregation occur simultaneously



Figure 3 - Possible mechanism for doping 3: Aggregation occurs before charge transfer

Chapter 3: Methods

Solution Preparation

Three 30 $\mu\text{g/mL}$ solutions of low molecular weight (LMW) P3HT were made in an airtight glove box. Reducing exposure to oxygen is important to eliminate the possible side reaction induced by the presence of oxygen, which would skew the experimental results. One solution was made using pure toluene as a solvent. The other two used differing ratios of decane in toluene, one 25% and the other 45%. Decane was chosen due to its properties as a bad solvent for P3HT, meaning its presence in the solution causes the polymer to aggregate very quickly since LMW P3HT is completely solubilized in toluene. It was also chosen due to its nonpolar qualities so it does not promote additional charge transfer. Each sample was made directly in a custom-made vacuum-safe cuvette with a bulb. Once the solution was in the cuvette, 20 μL (5 weight percent) of F4TCNQ was added to the bulb, being careful not to mix it with the solution prematurely.

Spectroscopic Analysis of Solutions

After being removed from the glove box, an ultraviolet-visible (UV-vis) spectrum was obtained for each P3HT-only solution using a Cary-60 spectrometer. The solutions were heated to 100°C for 30 min to make sure all P3HT was fully solubilized, then cooled back to room temperature. A UV-vis spectrum showing the aggregation peaks was obtained for each sample. The solutions were then immediately mixed with the dopant to further record the UV-vis spectra.

25% and 45% Decane Solutions

After mixing, the decane solutions were aged over two days to allow the doping product to form. Both morphological forms of P3HT are shown in Figure 4. The solutions were then heated to 100°C to resolubilize the polymer and then cooled again to room temperature. A spectrum was then taken of the doped solution.



Figure 4 - (left) solubilized P3HT; (right) aggregated P3HT

Pure Toluene Solution

Because LMW P3HT is fully soluble in toluene, a different method was necessary to test for doping. Instead of waiting two days to allow for aggregation, the UV-vis spectrophotometer was set to continually take spectra of the toluene solution over the course of three days.

Chapter 4: Results and Discussion

Spectroscopic Data for Decane Solutions

When interpreting UV-vis spectra for a doping reaction, it is important to identify the main doping peaks. The peak for the solubilized form of P3HT, s-P3HT, is around 450 nm. The aggregation peaks for the aggregated products, the nanowire form of P3HT (nw-P3HT) appear around 610 nm and 560 nm. The peaks designating the doping product, or the result of the charge transfer reaction between polymer and dopant, appear between 750 and 850 nm. These are clearly visible in Figure 5.

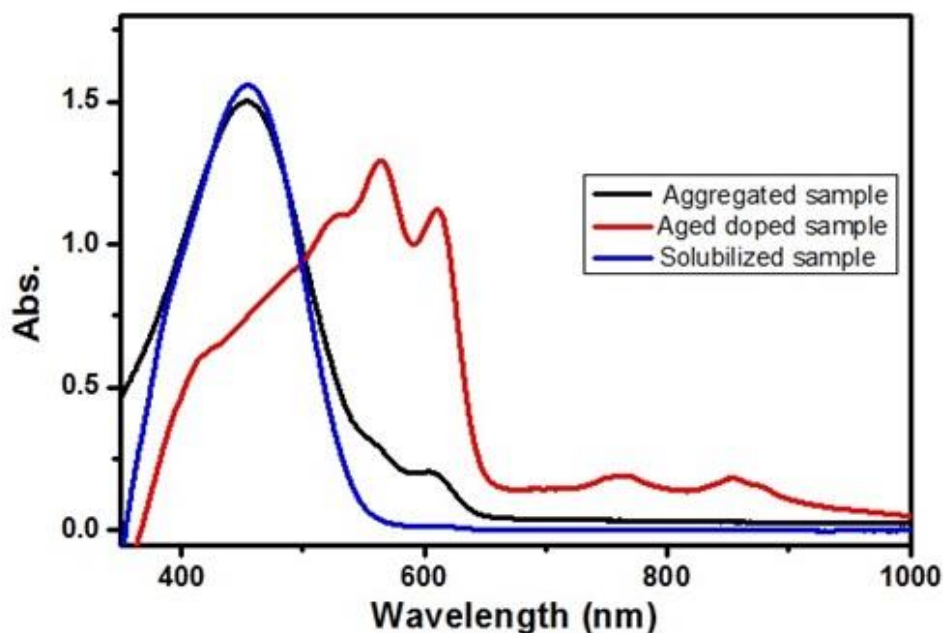


Figure 5 - UV-vis spectrum of 25% decane solution: fully solubilized sample shown in blue, freshly aggregated sample in black, and the fully doped sample in red.

It is clear from the spectra of the aggregated sample that as the nw-P3HT peak rises, the s-P3HT peak becomes smaller. This shows the balance that exists between the different morphological forms of P3HT, as illustrated in the first step of Figure 3. It can

also be seen that a larger amount of nw-P3HT gives rise to a larger amount of doping product. The same phenomenon is observed in the spectrum for the 45% decane solution, as shown in Figure 6.

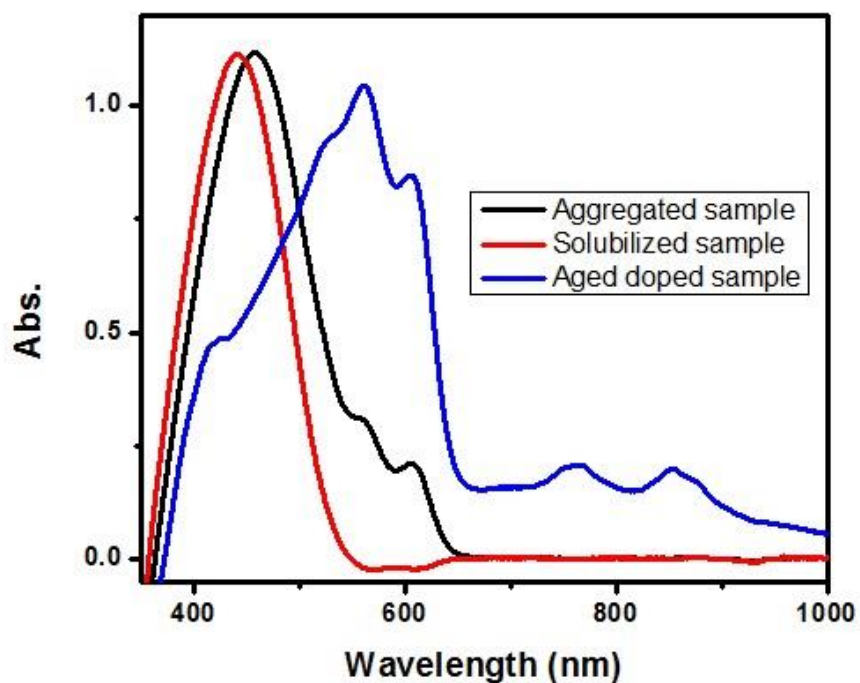


Figure 6 - UV-vis spectrum of 45% decane solution: fully solubilized sample shown in red, freshly aggregated sample in black, and fully doped sample in blue.

Pure Toluene

The spectra for the decane solutions should be compared to the UV-vis data for the solution in pure toluene, shown in Figure 7.

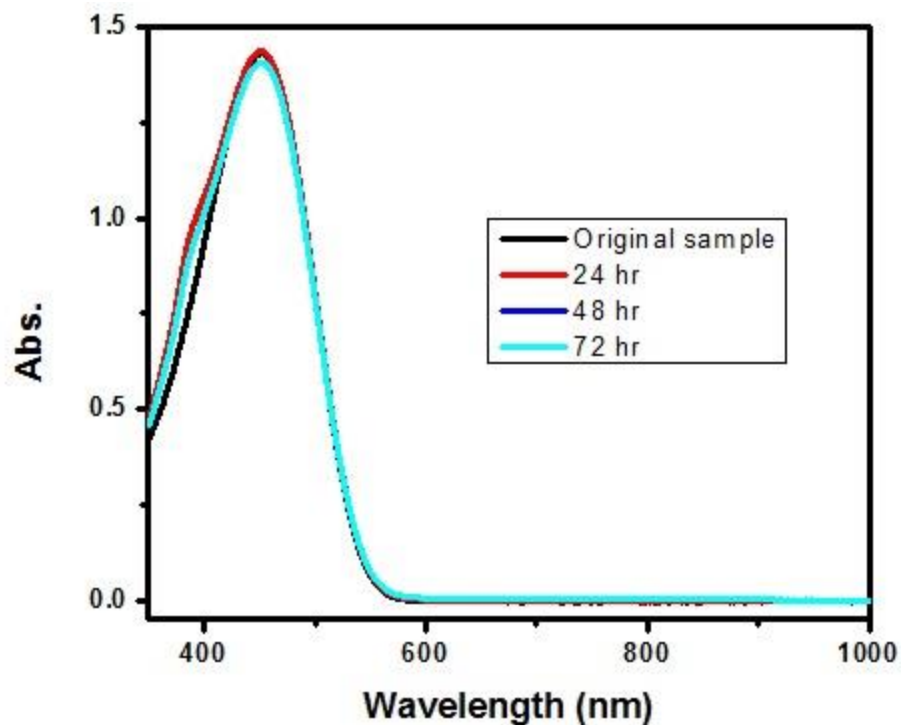


Figure 7 - UV-vis spectrum for pure toluene solution: original solubilized sample shown in black, 24 hour spectrum in red, 48 hour spectrum in dark blue, and 72 hour spectrum in light blue.

It is apparent from the spectrum that there was no aggregation and no doping in the pure toluene solution. LMW P3HT dissolves easily in toluene and remains in solubilized form at room temperature for days. The addition of the F4TCNQ dopant leads to the shoulder peak at approximately 390 nm. For a more complete picture, this spectrum can be compared to the spectrum for high molecular weight (HMW) P3HT, shown in Figure 8. HMW P3HT can easily aggregate in toluene, and similar to the results in Figure 5 and Figure 6, the emergence of aggregate peaks is accompanied by the formation of doping products.

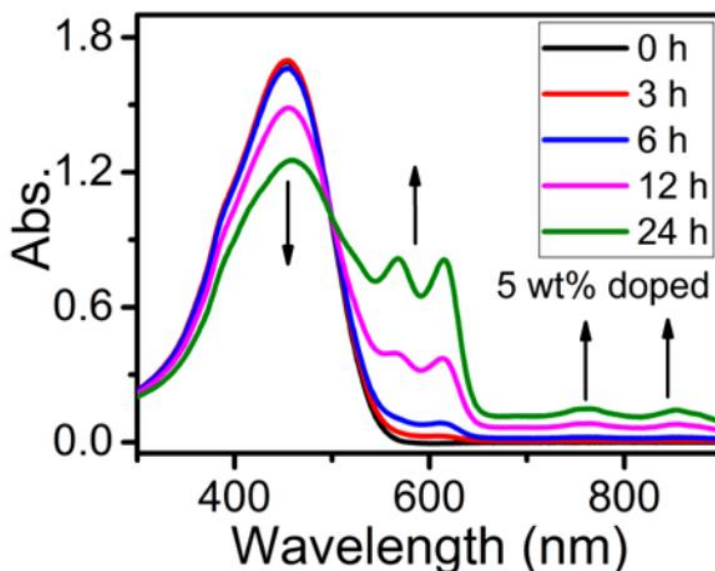


Figure 8 - UV-vis spectrum of HMW P3HT in pure toluene¹⁴: original solubilized sample shown in black, 3 hour spectrum in red, 6 hour spectrum in blue, 12 hour spectrum in pink, and 24 hour spectrum in green.

Based on the data obtained, one can see a clear correlation between the presence of aggregation peaks and the presence of doping peaks. In pure toluene, LMW P3HT does not aggregate, and there are no doping products formed even after 5 wt% F4TCNQ dopant was added for 72 h. This indicates that fully solubilized P3HT likely does not undergo charge transfer with F4TCNQ, which is contradictory to the mechanism 1 proposed in Figure 1 and the mechanism 2 proposed in Figure 2. In the two decane-toluene solutions, a large amount of nw-P3HT was formed, and a significant amount of doping product was also formed. Similarly, when the spectrum for LMW P3HT in pure toluene is compared with the spectrum of HMW P3HT in pure toluene, it is observed that when the polymer can aggregate, a doping product forms. Over the course of 24 hours, significant doping product is observed in the HMW sample, while the LMW displays no doping product after 72 hours without aggregation.

This correlation gives evidence to support the hypothesis that in the doping reaction between P3HT and F4TCNQ, the aggregation step must occur before the charge transfer step, as in mechanism 3 proposed in Figure 3. If the charge transfer step occurred before or at the same time as the packing step, doping product peaks would appear regardless of the ability of the polymer to aggregate. This suggests that the missing aggregation step for the LMW sample in pure toluene results in a significant barrier to the doping process.

Chapter 5: Conclusions

Our results demonstrate that the mechanism shown in Figure 3 of this thesis is, in fact, the most likely mechanism for the doping of P3HT using F4TCNQ. Further research could be done to test LMW P3HT in toluene at a temperature that allows aggregation to occur to see if doping is possible once that aggregation barrier is lifted. The kinetic effect of F4TCNQ on pre-formed nw-P3HT as opposed to letting the sample aggregate with the dopant already mixed in could also be investigated. These studies would give even more insight into the mechanism and the direct kinetic effect of the polymer's packing on the doping process, which could lead to better kinetic control of chemical doping processes for the fabrication of conjugated polymer-based devices.

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